Glycol/Ether Analysis
By Direct Aqueous Injection-GC/MS analysis

Summary:

This procedure is based on Restek Application Note 59187 located in Attachment 1 using a mass spectrometer instead of an FID.

Water samples are analyzed by direct injection into a gas chromatograph with a wax column followed by full scan electron impact mass spectrometry. Soil/sediment samples are extracted for 1 hour with reagent water in a sonication water bath and decanted prior to analysis as waters.

Target Analytes	CAS #
2-Butoxyethanol	111-76-2
Propylene glycol	57-55-6
Di(propylene glycol) butyl ether	29911-28-2

Analytical Equipment and Conditions:

Agilent 7890 Gas Chromatograph and 5975 Mass Spectrometer
Drilled double gooseneck Uniliner (installed with hole at top) cat # 20509
Restek Stabilwax column 30m x 0.32mm ID x 1um film cat #10654

See specific GC conditions in Figure 2 of Attachment 1.

Mass spec is operated in full scan electron impact mode, scanning from mass 35 to 250 amu with approximately 6 scans/second.

Calibration:

The following calibration points are used:

0.5, 1, 2, 5, 10, 25, 50, 100, 150, 200 ug/ml of all 3 target analytes prepared in reagent water. No internal standards or surrogates are used for this procedure. Stock standard solutions were prepared at 10 mg/ml in MeOH from neat solutions.

Calibration for the Di(propylene glycol0 butyl ether is based on summing the two larger isomers present and calibrating using the total area.

Procedure:

To prepare aqueous QC, 100 ug of each target is added to 1 ml of reagent water for blank spike and to two 1ml duplicate aliquots of a sample for matrix spikes. Reagent water is used for the blank. All aqueous samples and QC are direct injected into the GC with no

additional sample preparation. To increase lifetime of the injection port liner, filtration may be used. Note: Due to carryover in the system, spiked samples are analyzed after calibration check and prior to blanks. Blanks are then analyzed twice prior to analysis of samples to ensure that carryover is minimal. Twelve syringe washes using 1:1 water/MeOH are used between each run.

Soil/sediment samples are extracted in a sonication water bath at ambient temperature for 1 hour. 10 g of each sample, blank and blank spike are weighed into screw cap vials. Ottawa sand is used for blank and blank spike. Two additional aliquots of a sample are weighed for matrix spikes. 1000 ug of all targets are added to blank spike, matrix spike, and matrix spike duplicate. 10 ml of reagent water are added to all samples and QC. Extraction by sonication water bath is allowed to proceed for 1 hour. Samples were allowed to settle for 10 minutes and a small portion of the extract is removed for analysis as a water. Additional centrifugation may be necessary to separate solids from water prior to analysis.

Quality Control:

Default quality control criteria from Method 8270 D were used for this procedure:

-20% RSD limit to use average response factor for calibration. 0.99 R or R^2 used for linear or quadratic curve fits
- ±20 % criterion used for continuing calibration check
- Blank concentration is less than RL; sample concentrations ≤10 x blank concentration are qualified as blank related.
-70-130 % limits used for blank spike and matrix spikes with 30% RPD limit for duplicates
-No tune check is performed due to DFTPP instability in solutions other than Methylene chloride

Attachment 1

RESTEK environmental

#59187

Applications note

Techniques to Optimizing GC Analysis of Ethylene Glycol in Water

The analysis of ethylene glycol in water is a very common test in environmental laboratories. Many of these samples originate from water runoff at airports where ethylene glycol is used as a de-icing agent for airplanes during winter months. Because ethylene glycol is highly soluble in water, it is not easily concentrated by purge and trap. Therefore, the most frequently used sample introduction technique is direct aqueous injection. The direct aqueous injection of ethylene glycol can be challenging because, if not done properly, it can be difficult to attain reproducibility and good peak shape. The large expansion volume of water can cause backflash, carryover can cause inconsistent results, and excess water can extinguish the FID flame. These problems can prevent achieving the detection limit for ethylene glycol, which may vary in the 1-10ppm range.

Poor Peak Shape

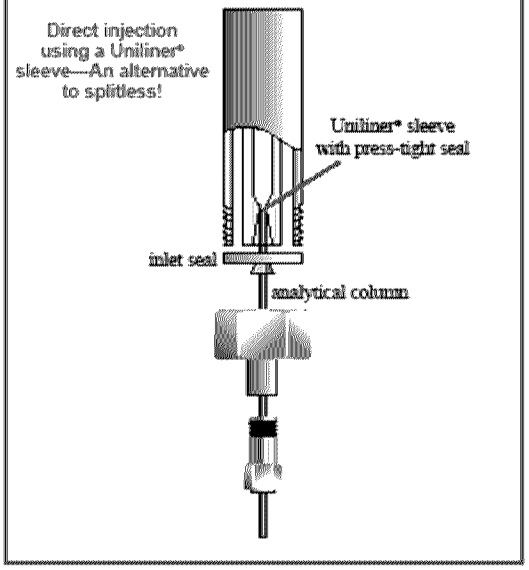
With a column head pressure of 10psig and an injection port temperature of 250°C, a 1µL injection of water will expand to 1420µL of vapor. This large vapor cloud exceeds the volume of most inlet liners, causing backflash. If backflash occurs, the vapor cloud can expand out of the liner and injection port and result in poor sample transfer onto the column. Also, the glycol compounds are not focused in a narrow band but, instead, are focused in the condensed water that beads onto the column walls, so the compounds of interest can elute as split peaks. This peak splitting effect is most apparent when performing a splitless injection because of the solvent focusing required. Split peaks and backflash compromise the analysis by causing irreproducible peak shapes.

One technique to reduce the effect of vapor expansion and poor solvent focusing is the use of a Uniliner® injection port sleeve. This sleeve forms a leak-free connection with the column end (**Figure 1**), thereby ensuring a complete sample transfer. Additionally, the Uniliner® sleeve requires operation at a higher pressure than traditional splitless liners, which forces the large vapor cloud to be focused into a narrow band when entering the column. This minimizes sample backflash and eliminates the need for solvent focusing. By using a Uniliner® sleeve, the aqueous ethylene glycol sample is completely vaporized and properly transferred to the column in a focused, narrow band, thereby achieving reproducible peak areas. Uniliner® sleeves are available for conversion of packed column injection systems and for split/splitless injection systems.

Sample Residue Carryover

Carryover is another problem associated with ethylene glycol analysis. When analyzing glycols, carryover can be caused by sample residue in the syringe being carried over from one injection to another. If the syringe is not properly cleaned between analyses, carryover will cause inconsistent results.

Figure 1
The Uniliner® sleeve forms a leak-free connection, minimizes backflash, and helps focus the sample.



Rinsing the syringe with either water or water/methanol (50:50) three to six times between each injection will eliminate sample residue and minimize the possibility of carryover.

FID Flameout

Column stationary phase choice is a critical consideration when analyzing glycols in water via direct injection. Water analyzed on a non-polar stationary phase, such as the Rtx®-1 column, or on a moderately polar stationary phase, such as the Rtx®-200 column, will cause the flame on the FID to be extinguished. This is because the water will not partition properly and will "bead up" on the phase, producing a large plug of water that passes through the detector and extinguishes the flame. The more commonly-used GCs will experience flameout under these circumstances while others will not.

To minimize the possibility of extinguishing the flame, select a polar stationary phase that is more compatible with water. The Stabilwax® stationary phase is one of the more polar phases, making it a good choice for water injections. It allows water to partition properly, which prevents it from beading up on the stationary phase and quenching the FID flame.

environmental

The Stabilwax® column can easily handle direct aqueous injections without showing any signs of degradation. Testing of the Stabilwax® column was performed by injecting 1µL of a water standard 100 times. Peak shape and response of ethylene and propylene glycol remained consistent throughout the analyses (**Figures 2 and 3**). The Stabilwax® column also allows sensitive detection of low ppm-levels of glycol compounds. Notice the 5ppm detection limit for ethylene glycol in water is easily achieved, and peak shape is maintained when compared to a 25ppm standard (**Figure 4**).

Conclusion

You can achieve better response and reproducibility for the GC analysis of ethylene glycol in water by using direct injection with a Uniliner® sleeve, a polar capillary column such as Stabilwax®, and multiple syringe washes between runs. Using these techniques can assist in attaining reproducible analyses with detection limits in the low ppm range.

Figure 2
The Stabilwax® column shows good peak shape and response for ethylene glycol after 100 injections.

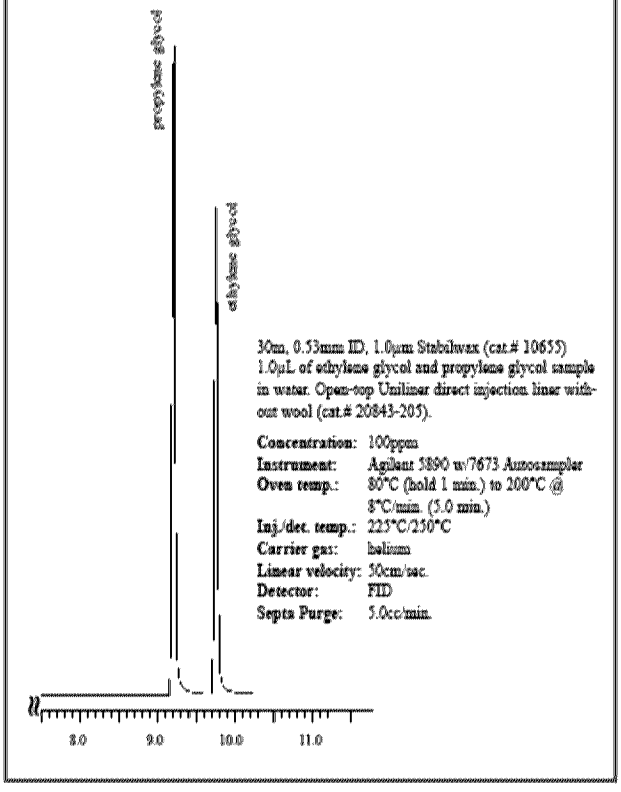


Figure 3
The Stabilwax® column combined with a Uniliner® sleeve shows remarkable response consistency.

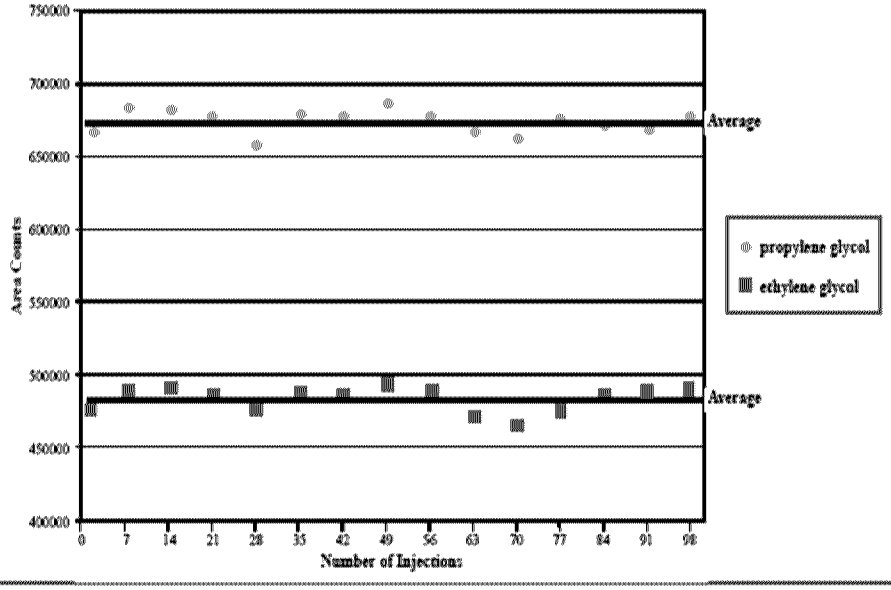
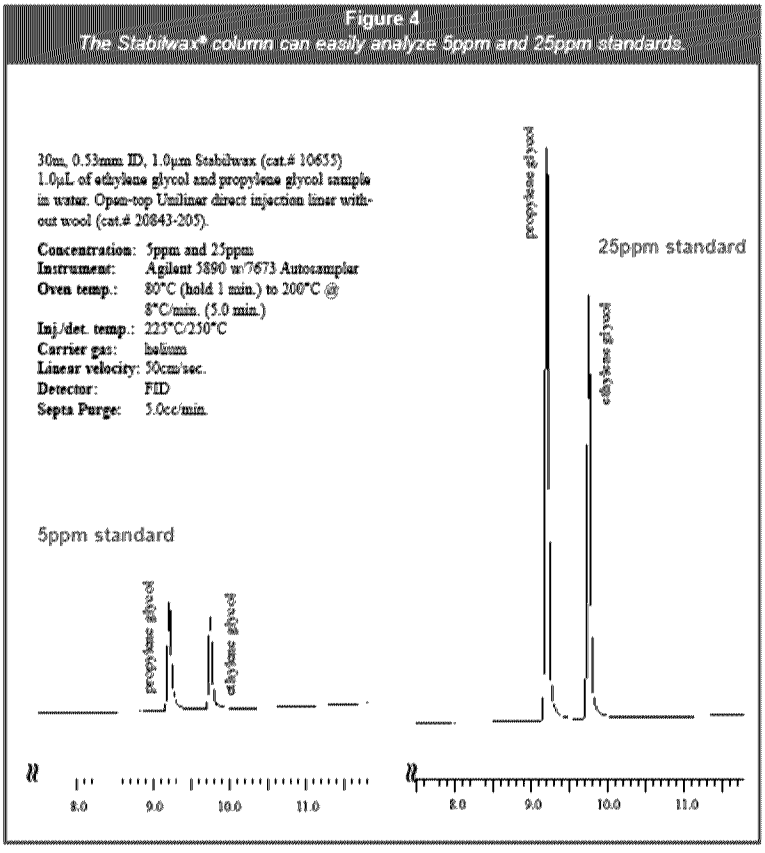


Figure 4
The Stabilwax® column can easily analyze 5ppm and 25ppm standards.



Product Listing:

Stabilwax® Columns

30m	0.32mm ID	1.0µm	cat.# 10654
30m	0.53mm ID	1.0µm	cat.# 10655

Uniliner® Sleeves

Description	Column ID Inj. Mode	Each*	5-pack
***Uniliner® Sleeve** (large buffer volume chamber—85mm long for injections ≤4µL)*	0.32 & 0.53mm DI only	20308	20309
	0.53mm DI or OC	20301	20305
***Cyclo-Uniliner® Sleeve** (for active dirty samples)*	0.32 & 0.53mm DI only	20319	20320
***Open-Top Uniliner® Sleeve** (packed with fused silica wool)*	0.32 & 0.53mm DI only	20315	20316
***Uniliner® Sleeve Adaptor** (required for installing Uniliner® sleeves in ¼" injection ports)*	*includes a ¼" SS nut and graphite ferrule, a 4/40" SS nut, and a 0.8mm ID graphite ferrule.*		
	***For injection ports <8cm:** cat.# 20310 ea.*		
	***For injection ports 8-15cm:** cat.# 20311 ea.*		
	***For Shimadzu:** cat.# 20312 ea.*		

**Add the suffix "-205" to the catalog number to order without wool.*

continued on back

Product Listing, continued:

Uniliner® Sleeves

Direct Injection Liners for Agilent & Finnigan GCs *(0.32/0.53mm ID)*	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Uniliner®	trace, active samples, high recovery & linearity	4.0 ID, 6.3 OD x 78.5	20335	20336
Cyclo-Uniliner®†	trace, dirty, high MW active samples, high recovery & linearity	4.0 ID, 6.3 OD x 78.5	20337	20338
Open-top Uniliner® with Wool	trace, dirty active samples, high recovery & linearity	4.0 ID, 6.3 OD x 78.5	20843	20844

Direct Injection Liners for Agilent 6890 GCs *(0.32/0.53mm ID)*	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Drilled Uniliner®	allows direct injection when using an EPC-equipped GC	4.0 ID, 6.3 OD x 78.5	21054	21055

Direct Injection Liners for Varian GCs *(0.32/0.53mm ID)*	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Uniliner®	trace, active samples, high recovery & linearity	4.0 ID, 6.3 OD x 72	20345	20346
Cyclo-Uniliner®	trace, dirty, high MW, active samples, linearity	4.0 ID, 6.3 OD x 72	20347	20348
Open-top Uniliner® w/ Wool*	trace, dirty, active samples, high recovery & linearity	4.0 ID, 6.3 OD x 72	20845	20846

Direct Injection Liners for Shimadzu GCs *(0.32/0.53mm ID)*	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
128mm Uniliner®	trace, active samples, high recovery & linearity	3.0 ID, 5.0 OD x 128	20872	20873
128mm Cyclo-Uniliner®	trace, dirty, high MW active samples, linearity	3.5 ID, 5.0 OD x 128	20874	20875
99mm Uniliner®	trace, active samples, high recovery & linearity	3.0 ID, 5.0 OD x 99	20876	20877
99mm Cyclo-Uniliner®	trace, dirty, high MW active samples, high recovery & linearity	3.0 ID, 5.0 OD x 99	20893	20894
94mm Uniliner® w/ Wool*	trace, dirty, high MW active samples, high recovery & linearity	3.0 ID, 5.0 OD x 94	21713	21719

Direct Injection Liners for Perkin-Elmer GCs *(0.32/0.53mm ID)*	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Uniliner®	trace, active samples, high recovery & linearity	3.5 ID, 5.0 OD x 100	20855	20856
Cyclo-Uniliner®	trace, dirty, active samples, linearity	3.5 ID, 5.0 OD x 100	20857	20858
Auto SYS Open-top Uniliner® w/ Wool*	trace, dirty, active samples, high recovery & linearity	4.0 ID, 6.2 OD x 92.1	20837	20838
Auto SYS Cyclo-Uniliner®	trace, dirty, high MW active samples, linearity	4.0 ID, 6.2 OD x 92.1	20839	20840

Split Liners for 5000-6000 Series GCs	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Open-top Uniliner® w/ Wool*	trace, dirty, active samples, high recovery & linearity	4.0 ID, 5.5 OD x 79.5	20841	20842

Direct injection Liners for 8000 & TRACE™ Series GCs	Benefits/Uses:	ID***/OD & Length (mm)	Each*	5-pack
Uniliner® w/ Wool	trace, active samples, high recovery & linearity	5.0 ID, 8.0 OD x 105	21005	21006

**Add the suffix "-205" to the catalog number to order without wool.*
***These liners are packed with fused silica wool. To order glass wool instead, add the suffix "-202" to the liner's catalog number.*
****Nominal ID at syringe needle expulsion point.*
†These Uniliner® sleeves are for split/splitless injection ports.

USA: 110 Benner Circle, Bellefonte, PA 16823 • phone: (800) 356-1688 • fax: (814) 353-1309
Germany: Schaberweg 23, 61348 Bad Homburg • phone: (49) 06172-2797-0 • fax: (49) 06172-2797-77
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